

## Supporting Information

### Synthesis and Structure of Bis(diphenylphosphinimino)methanide and Bis(diphenylphosphinimino)methanediide Beryllium Complexes.

*Melike Bayram, Dominik Naglav, Christoph Wölper, Stephan Schulz\**

Institute of Inorganic Chemistry, University of Duisburg-Essen, 45117 Essen, Germany

#### Table Content

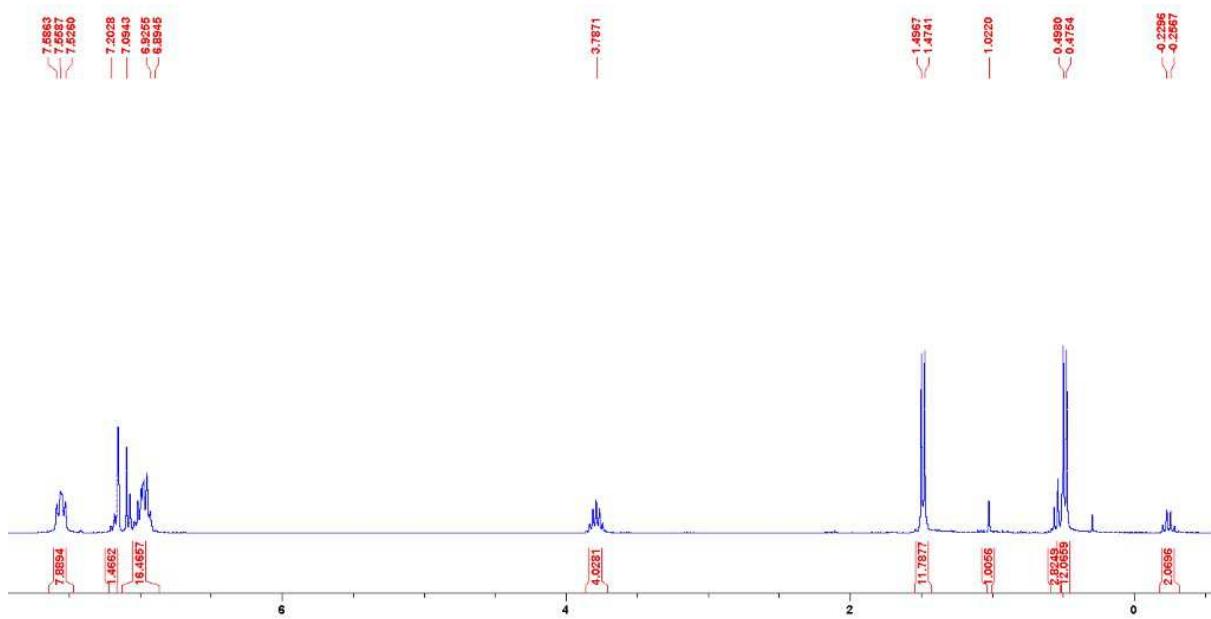
**Fig. S1 - S5:**  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^9\text{Be}$  NMR and IR spectra of **1**.

**Fig. S6 - S10:**  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^9\text{Be}$  NMR and IR spectra of **2**.

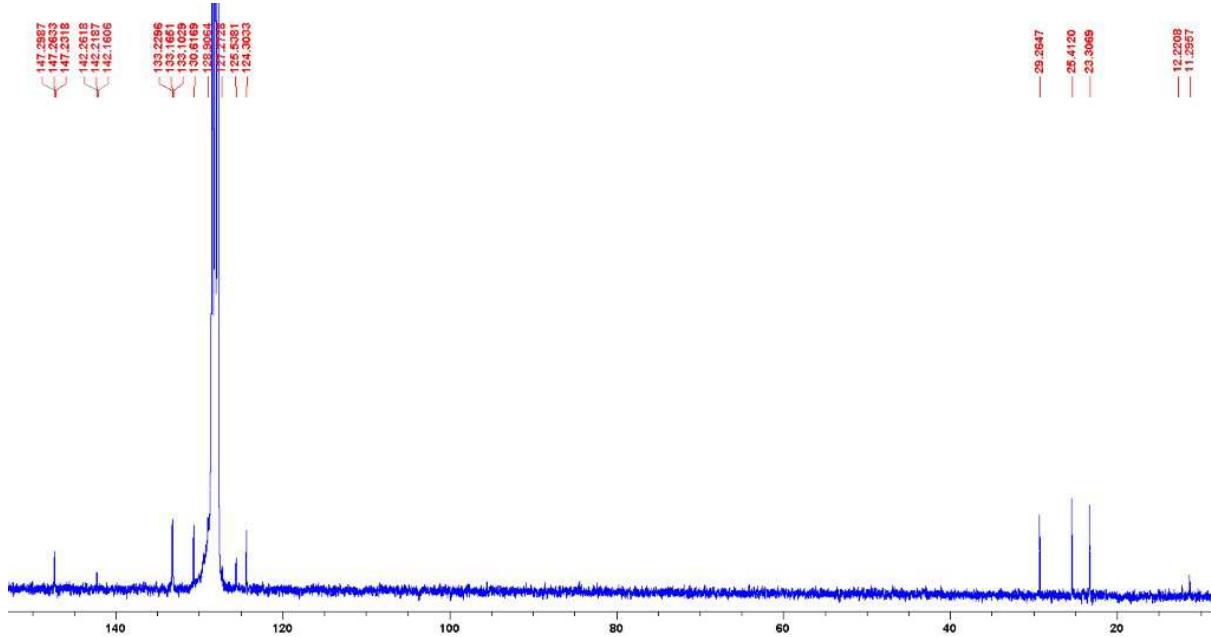
**Fig. S11 – S15:**  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^9\text{Be}$  NMR and IR spectra of **3**.

**Table S1.** Crystallographic details for complexes **1 - 3**.

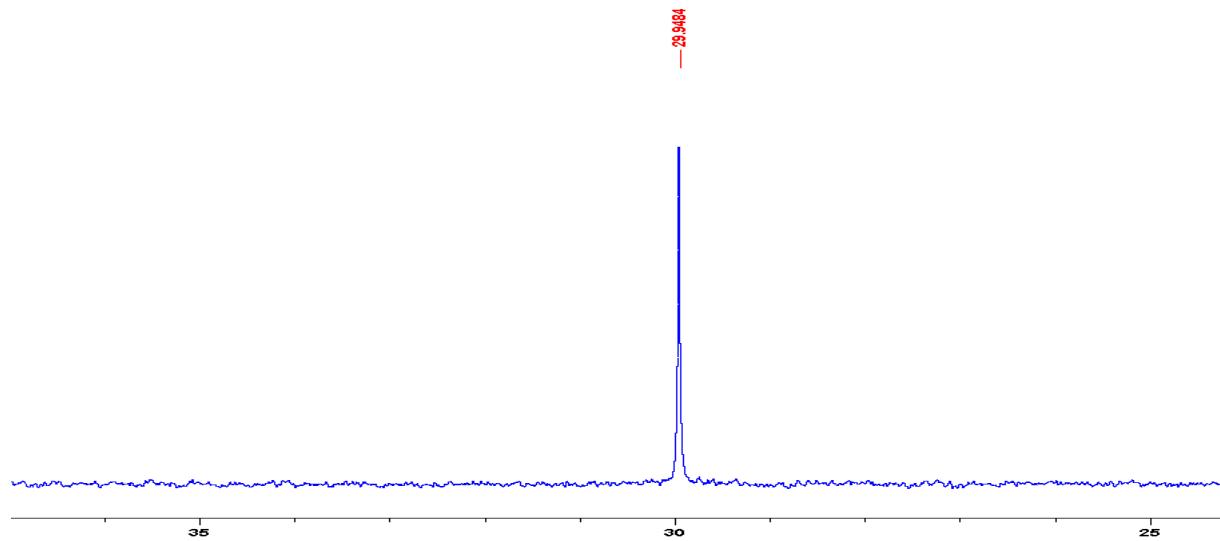
**Figure S1.**  $^1\text{H}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ , chemical shift in ppm.



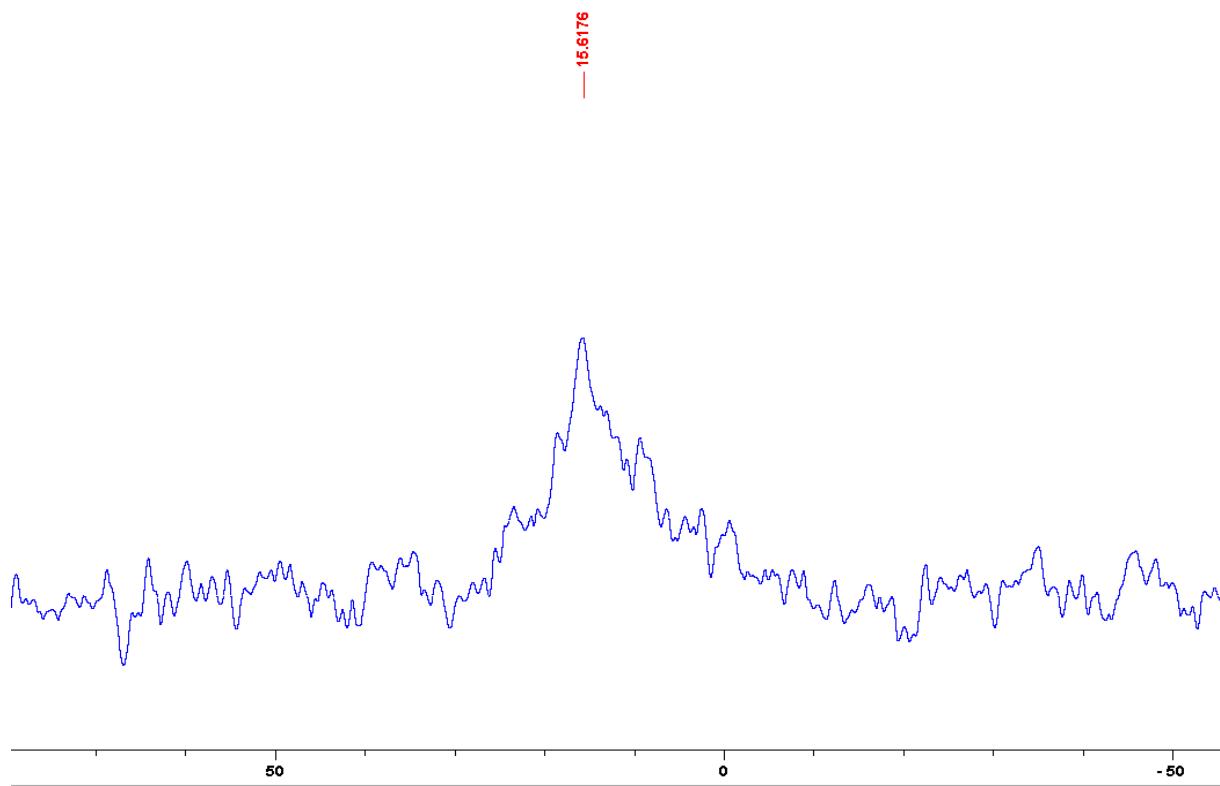
**Figure S2.**  $^{13}\text{C}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ , chemical shift in ppm.



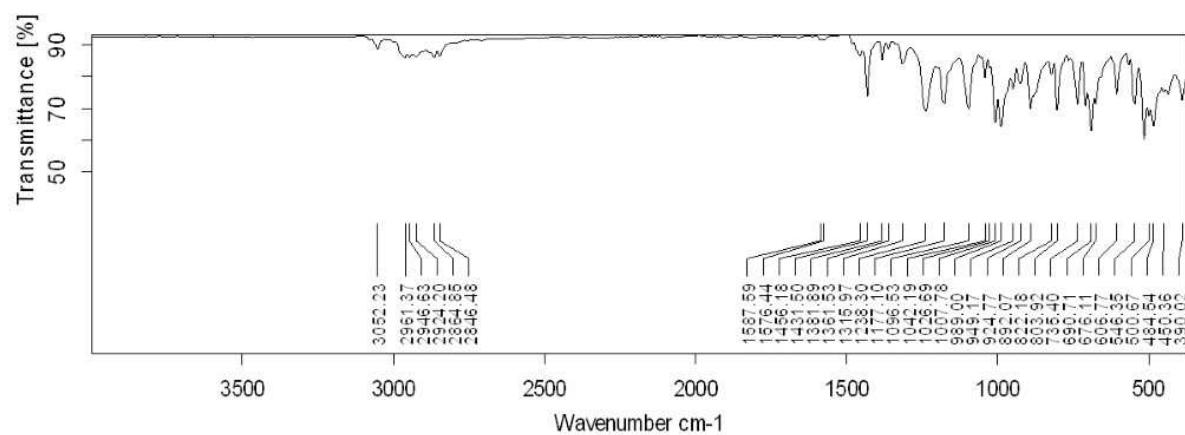
**Figure S3.**  $^{31}\text{P}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ , chemical shift in ppm.



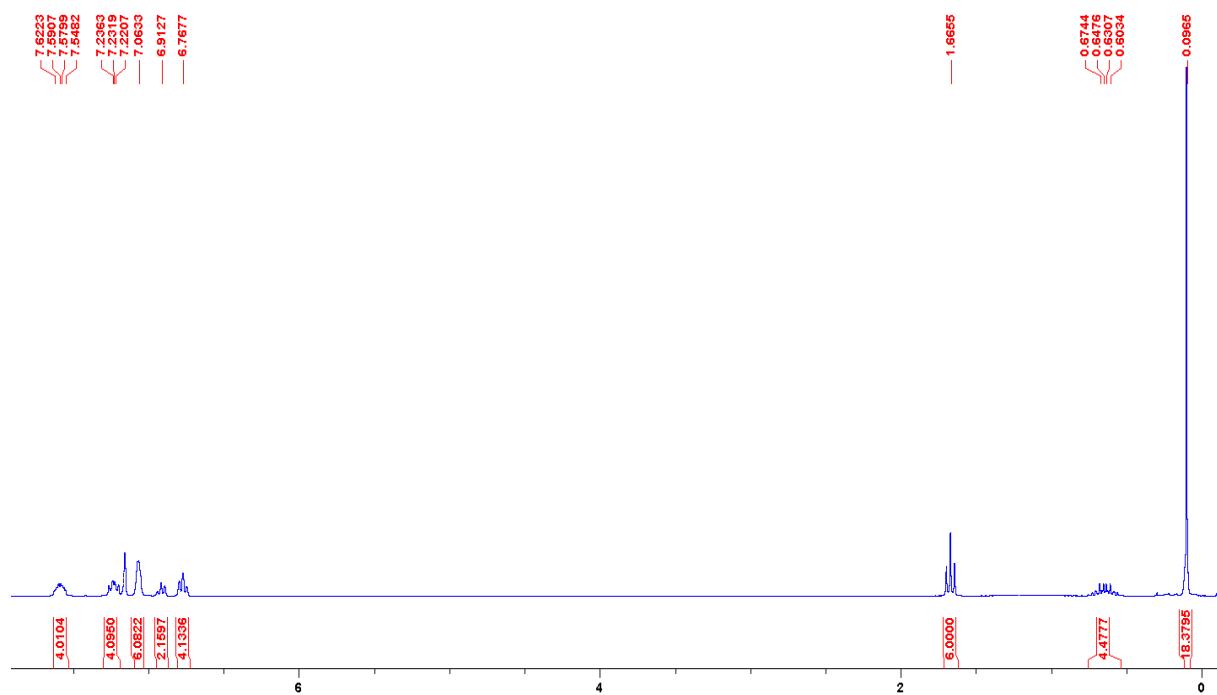
**Figure S4.**  $^9\text{Be}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ , chemical shift in ppm.



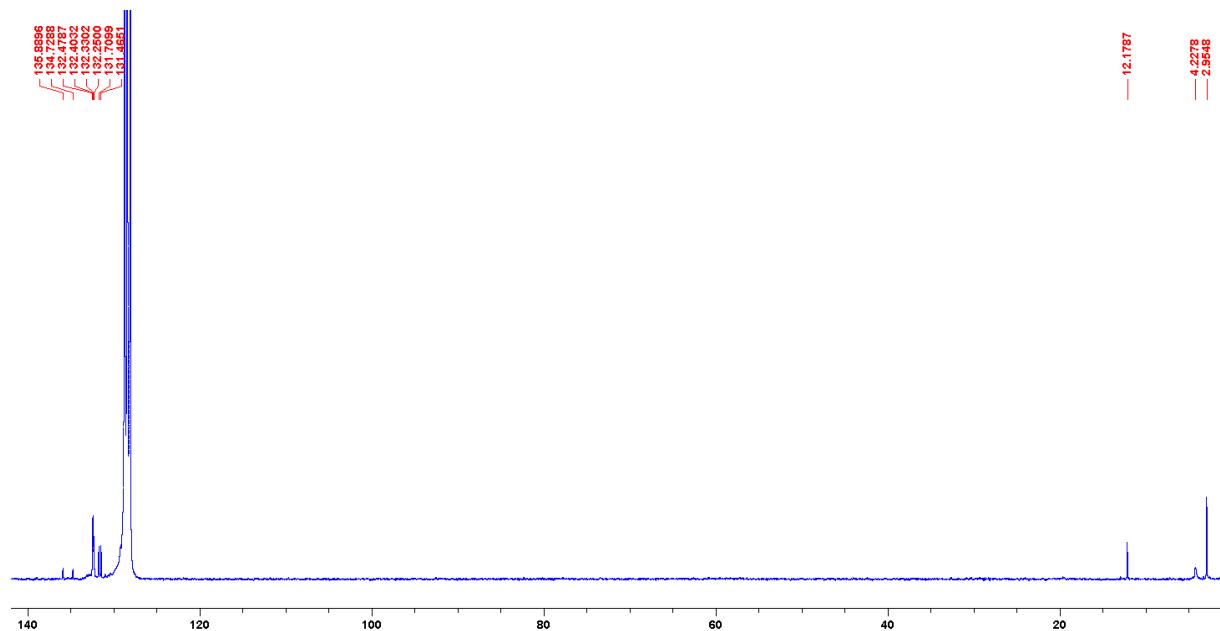
**Figure S5.** ATR-IR spectrum of **1**.



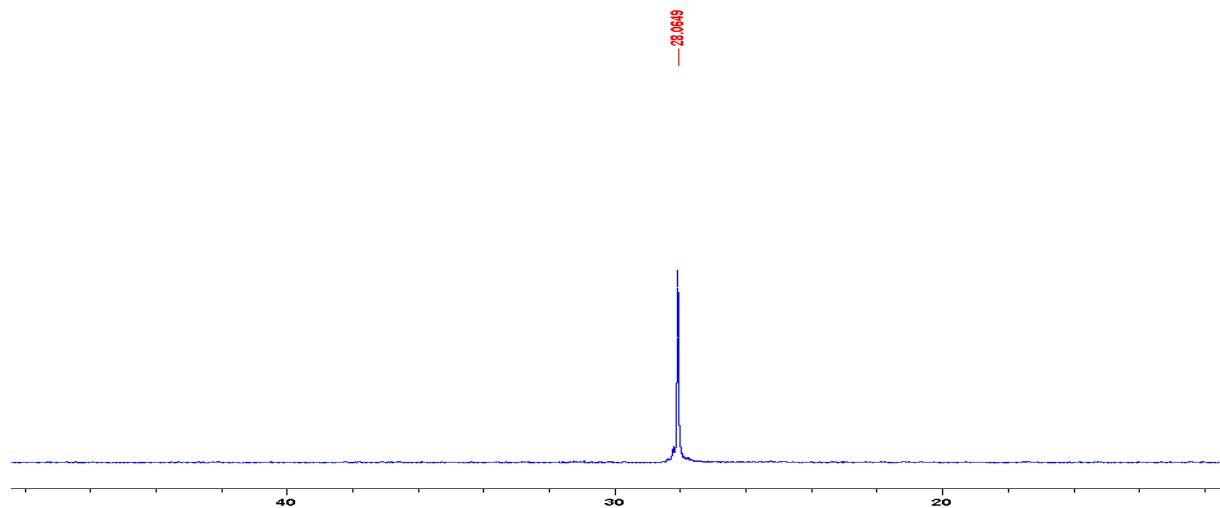
**Figure S6.**  $^1\text{H}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$ , chemical shift in ppm.



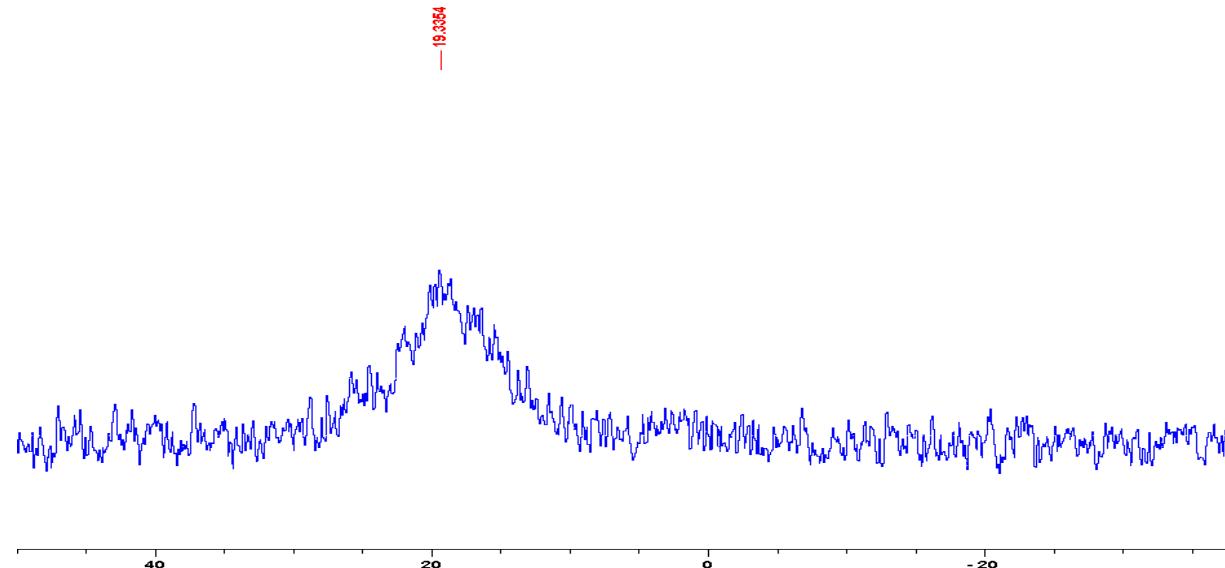
**Figure S7.**  $^{13}\text{C}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$ , chemical shift in ppm.



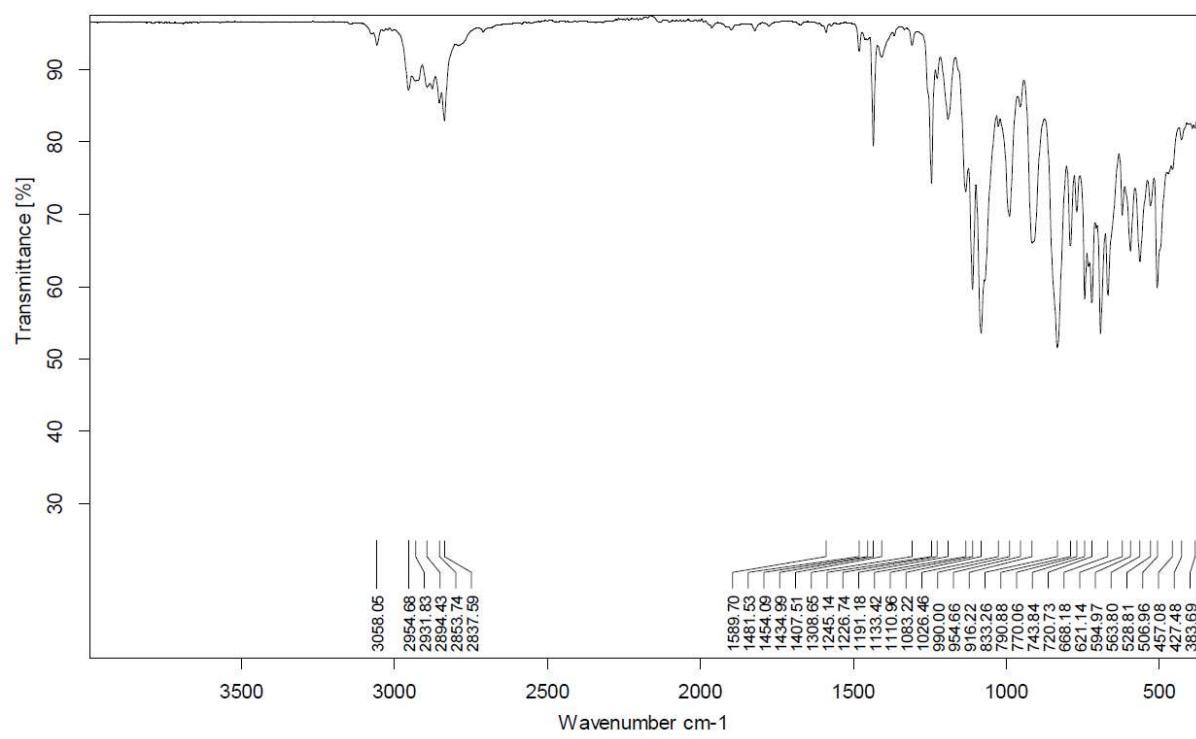
**Figure S8.**  $^{31}\text{P}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$ , chemical shift in ppm.



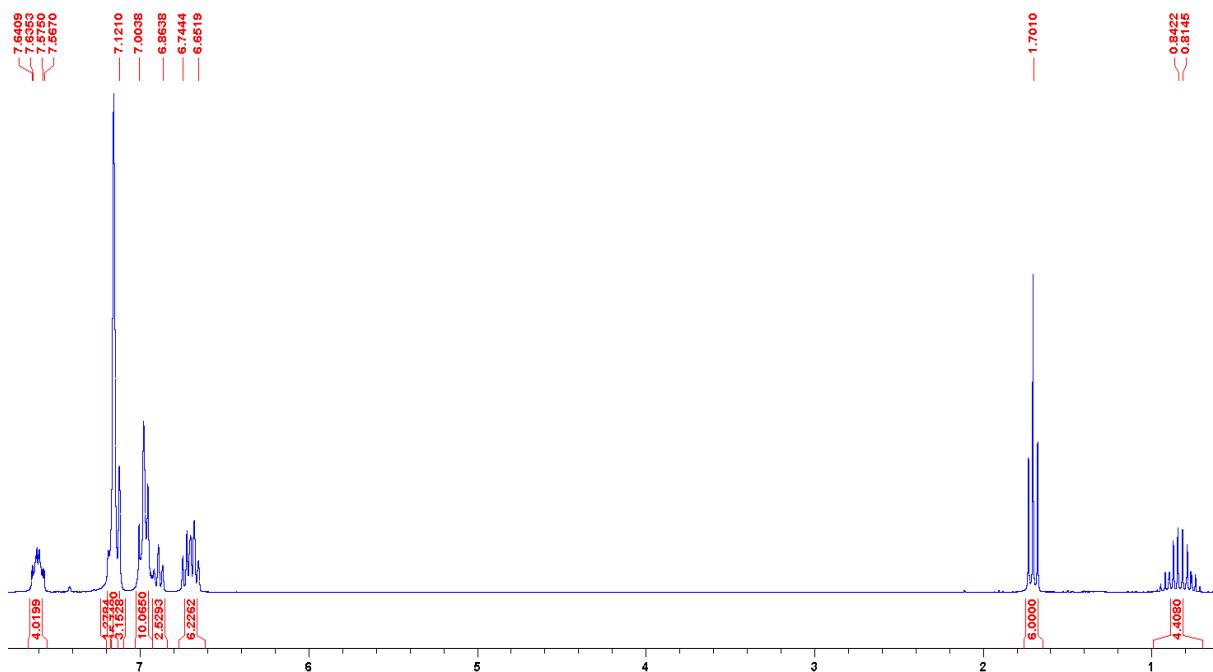
**Figure S9.**  $^9\text{Be}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$ , chemical shift in ppm.



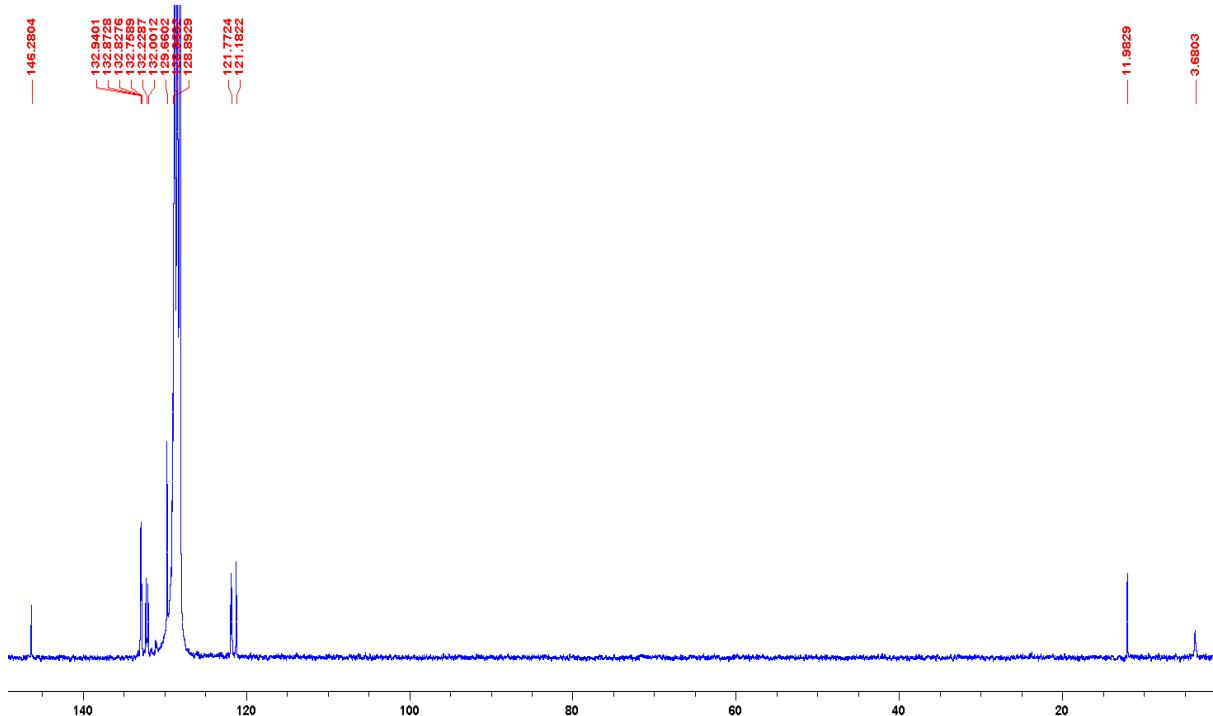
**Figure S10.** ATR-IR spectrum of **2**.



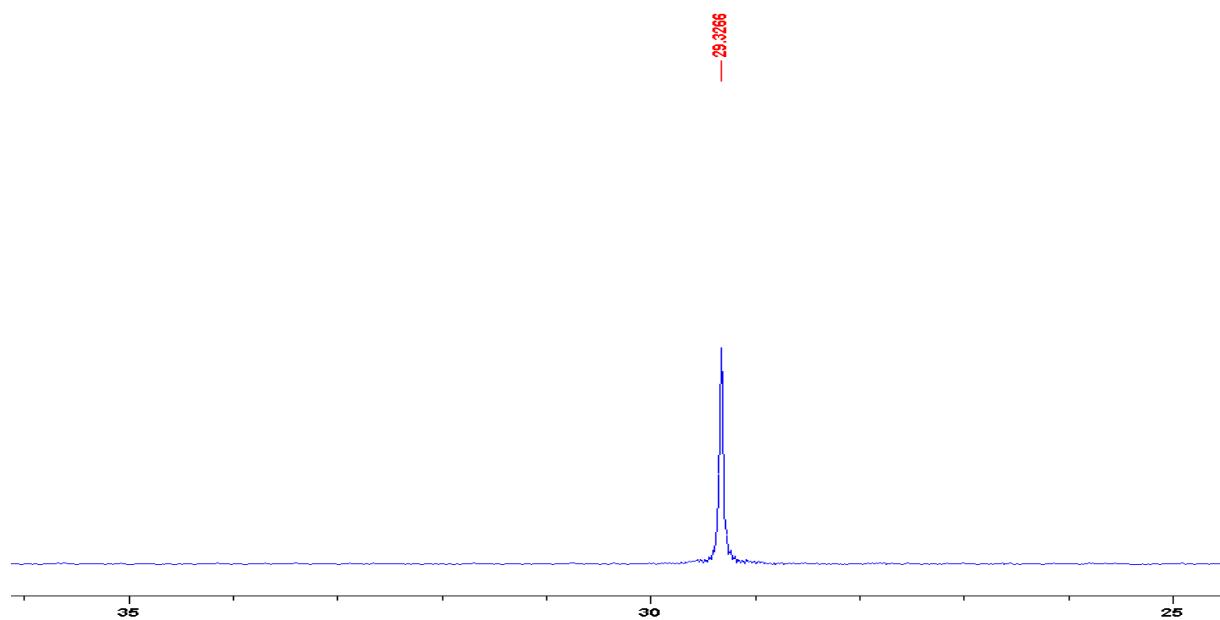
**Figure S11.**  $^1\text{H}$  NMR spectrum of **3** in  $\text{C}_6\text{D}_6$ , chemical shift in ppm.



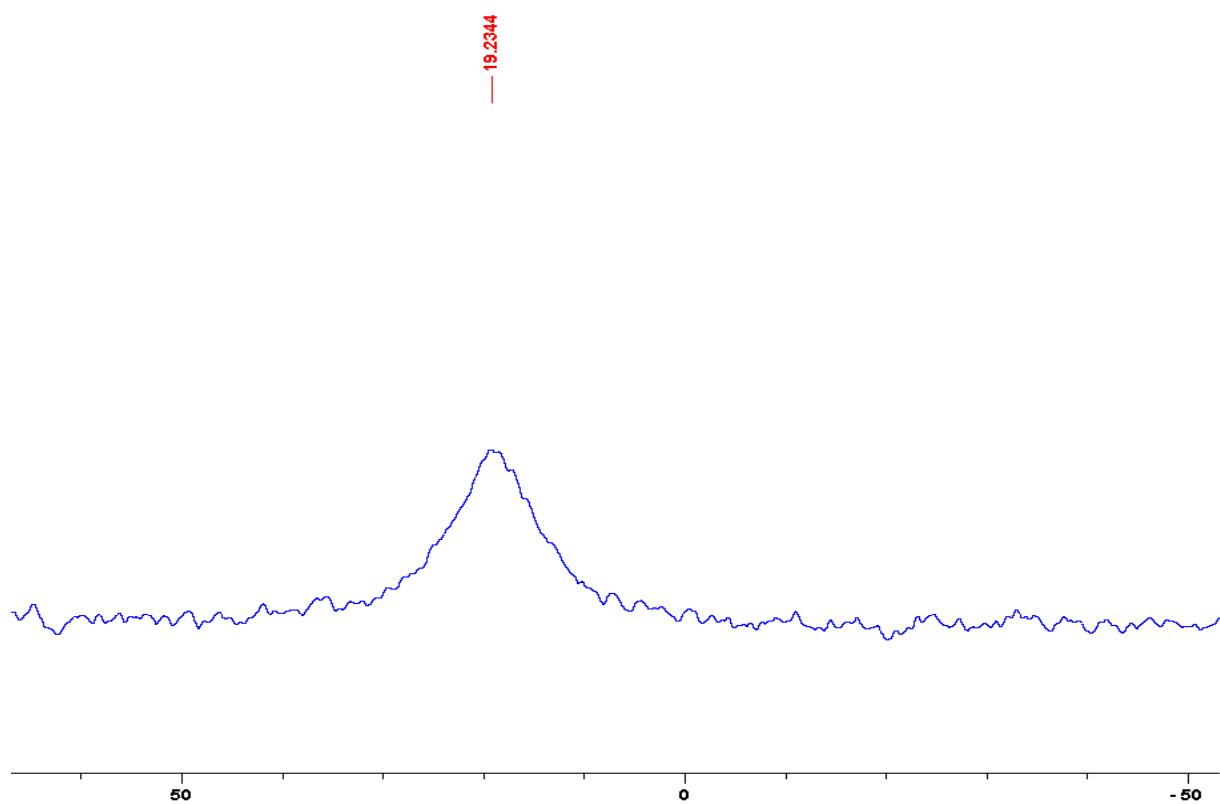
**Figure S12.**  $^{13}\text{C}$  NMR spectrum of **3** in  $\text{C}_6\text{D}_6$ , chemical shift in ppm.



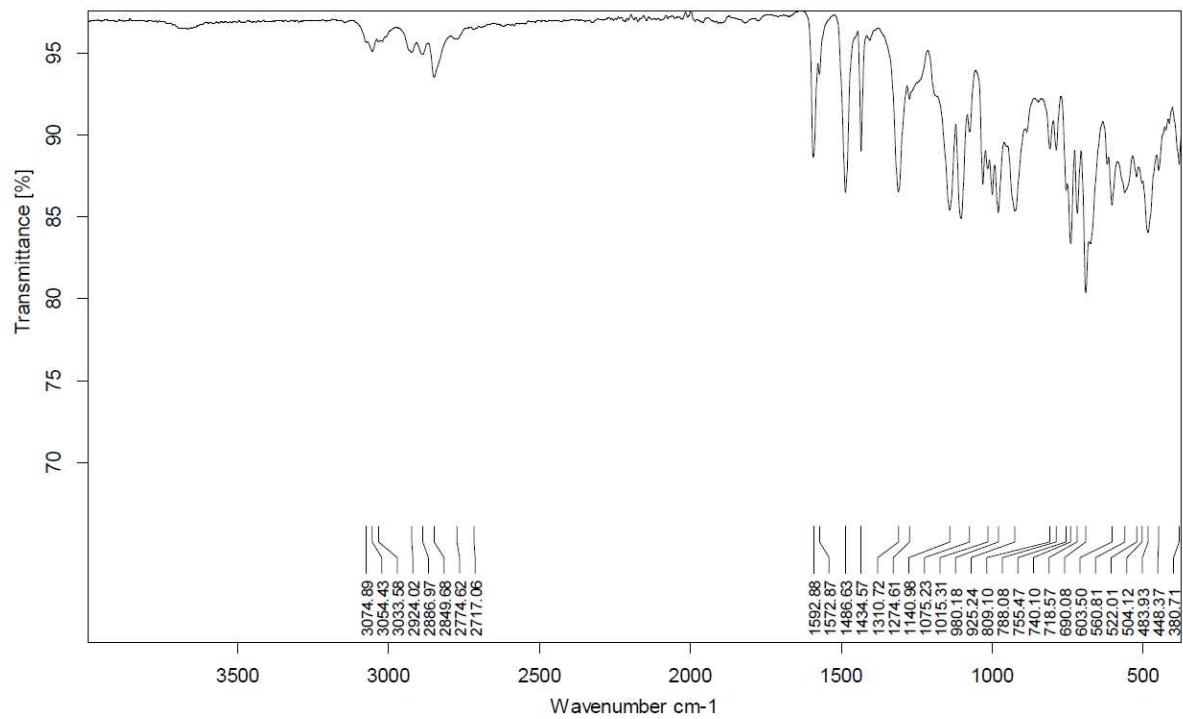
**Figure S13.**  $^{31}\text{P}$  NMR spectrum of **3** in  $\text{C}_6\text{D}_6$ , chemical shift in ppm.



**Figure S14.**  $^9\text{Be}$  NMR spectrum of **3** in  $\text{C}_6\text{D}_6$ , chemical shift in ppm.



**Figure S15.** ATR-IR spectrum of 3.



**Table S1. Crystallographic details of 1 - 3.**

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>51</sub> H <sub>60</sub> BeN <sub>2</sub> P <sub>2</sub>	C <sub>35</sub> H <sub>48</sub> Be <sub>2</sub> N <sub>2</sub> P <sub>2</sub> Si <sub>2</sub>	C <sub>41</sub> H <sub>40</sub> Be <sub>2</sub> N <sub>2</sub> P <sub>2</sub>
<i>M</i>	771.96	632.89	640.71
Crystal size [mm]	0.30 × 0.18 × 0.09	0.22 × 0.21 × 0.10	0.15 × 0.10 × 0.07
<i>T</i> [K]	100(1)	100(1)	100(1)
Crystal system	orthorhombic	triclinic	orthorhombic
Space group	<i>Pbca</i>	<i>P-1</i>	<i>Pbca</i>
<i>a</i> [Å]	17.6236(15)	11.4830(8)	19.0777(16)
<i>b</i> [Å]	20.2410(17)	17.7068(13)	17.7914(14)
<i>c</i> [Å]	24.665(2)	18.3945(15)	20.5506(17)
$\alpha$ [°]	90	90.41184)	90
$\beta$ [°]	90	91.935(4)	90
$\gamma$ [°]	90	90.137(4)	90
<i>V</i> [Å <sup>3</sup> ]	8798.5(13)	3737.9(5)	6975.3(10)
<i>Z</i>	8	4	8
<i>D</i> <sub>calc</sub> [g · cm <sup>-3</sup> ]	1.166	1.125	1.220
$\mu$ (MoK <sub>α</sub> [mm <sup>-1</sup> ])	0.135	0.205	0.156
Transmissions	0.75/0.38	0.75/0.64	0.75/0.61
<i>F</i> (000)	3312	1352	2704
Index ranges	0 ≤ <i>h</i> ≤ 24 0 ≤ <i>k</i> ≤ 29 0 ≤ <i>l</i> ≤ 35	-16 ≤ <i>h</i> ≤ 16 -24 ≤ <i>k</i> ≤ 25 -24 ≤ <i>l</i> ≤ 26	-24 ≤ <i>h</i> ≤ 26 -24 ≤ <i>k</i> ≤ 23 -28 ≤ <i>l</i> ≤ 29
$\theta_{\max}$ [°]	25.242	25.242	25.242
Reflections collected	13520	100197	76246
Independent reflections	13520	22272	10418
<i>R</i> <sub>int</sub>	0.1120	0.0359	0.0887
Refined parameters	514	792	426
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>[a]</sup>	0.0527	0.0603	0.0476
<i>wR</i> <sub>2</sub> [all data] <sup>[b]</sup>	0.1500	0.1629	0.1286
GooF <sup>[c]</sup>	1.085	1.066	1.021
Δ <i>ρ</i> <sub>final</sub> (max/min) [e · Å <sup>-3</sup> ]	0.531/-0.378	0.774/-1.040	0.464/-0.374

<sup>[a]</sup>  $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$  (for  $|I| > 2\sigma(I)$ ). - <sup>[b]</sup>  $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ . - <sup>[c]</sup> Goodness of fit =  $\{\sum[w(|F_o|^2 - |F_c|^2)^2]/(N_{\text{observns}} - N_{\text{params}})\}^{1/2}$ .  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$  with  $P = [F_o^2 + 2F_c^2]/3$ , *a* and *b* are constants chosen by the programme.